REMARKS

Anticipation Rejection of Claims 1 and 3

On page 2 of the Office Action, claims 1 and 3 are rejected under 35 U.S.C. 102(b) as being anticipated by Bost (US 3,963,571).

Applicants respectfully submit that the present invention is not anticipated by (or obvious over) Bost, and request that the Examiner reconsider and withdraw this rejection in view of the following remarks.

1) Bost discloses a **two-stage** reaction in which C_{18} α-hydroxycycloalkanone is dehydrated to form cyclooctadecenone, which is subsequently reacted with hydrogen to form cyclooctadecanone (reaction formulae (5) and (6) in the second column).

However, the method of the present invention is to conduct catalytically a dehydration reaction and a hydrogenation reaction simultaneously in a **single** pot in the coexistence of an acid catalyst and a hydrogenation catalyst and in the presence of hydrogen.

Accordingly, Applicants submit that the present invention is completely different from the method set forth in Bost, which conducts the two-stage reaction separately and sequentially.

2) The Examiner recognizes that a reaction conducted in the presence of zinc and hydrochloric acid is disclosed in Bost. However, this reaction disclosed by Bost and using zinc and hydrochloric acid is a reaction in which a cyclic α-hydroxyketone (cyclic acyloin) is reduced directly to a cyclic ketone (reaction formula (4) in the

second column), different from the reaction of the present invention, as discussed in detail subsequently in this response.

Further, Bost discloses in the specific description relating to the direct reduction using zinc and hydrochloric acid that, to 6.5 g (0.023 mol) of cyclic α-hydroxyoctadecanene, 10 g of zinc was first added under bubbling of hydrogen chloride, and further 2 g of zinc was added twice during reaction whereby 14 g (0.214 mol) of zinc in total was used for reaction (lines 50 to 65 of the fourth column). Namely, in the above reaction, 9.3 equivalents of zinc were used relative to acyloin as the raw material.

Moreover, in the attached reference material 1 (ORGANIC SYNTHESES VOL IV) that describes the reaction disclosed by Bost, relative to 42.5 g (0.25 mol) of sebacoin as a raw material, 40.5 g (0.62 mol) of zinc dust and 90 ml of concentrated hydrochloric acid were used at first, and that during reaction, an additional 90 ml of concentrated hydrochloric acid was added, so 180 ml (2.16 mol) of concentrated hydrochloric acid were used in total. These quantities calculate to give 2.5 equivalents of zinc and 8.64 equivalents of hydrochloric acid relative to one equivalent of sebacoin as a raw material. In addition, reference material 1 includes the expressions "remaining zinc" or "residual zinc", indicating that zinc is consumed during reaction.

As is evident from the descriptions of Bost and reference material 1 cited heretofore, in the direct reductive reaction using zinc and hydrochloric acid, the two compounds are **not** to be defined as "catalysts" by any means. In view of this fact,

the method of the present invention *in which a dehydration reaction is conducted catalytically and simultaneously with a hydrogenation reaction* is clearly different from the reaction set forth in Bost.

3) Further, the Examiner apparently considers that the reaction achieving direct reduction with use of zinc and hydrochloric acid and the one sequentially achieving dehydration and hydrogenation fall under a single reaction scheme. However, the reaction schemes for these two reactions are neither common to each other nor to be combined together.

For example, in the attached reference material 2 (COMPREHENSIVE ORGANIC TRANSFORMATIONS, R.C. Larock, Wiley-VCH, 1999), which collects a variety of reactions of conventionally known functional groups, such examples that zinc and/or hydrochloric acid act as catalysts are not set forth in the item for catalytic hydrogenation of alkenes.

Thus, it is evident that the reaction using zinc and hydrochloric acid cannot be applied to the hydrogenation reaction for a double bond, and that those skilled in the art have no motivation for combining these reactions. Moreover, Bost has no teaching or suggestion of the reaction of the present invention.

In particular, it is noted that the Examiner is combining elements of two separate, alternate processes in Bost and asserting that they are all present in a single process.

That is, Bost discloses at column 2, lines 36-42 "cyclic α-hydroxyketones (cyclic acyloin) which can be reduced directly to the cyclic ketones by hydrogen iodide or zinc and hydrochloric

acid. Alternatively, the cyclic acyloins can be dehydrated to the cyclic unsaturated ketones which can be selectively hydrogenated to the cyclic saturated ketone" (emphasis added).

Thus, Bost discloses the use of zinc and hydrochloric acid in one process (a direct reduction process), and the use of dehydration and then hydrogenation is a different, alternate process. Bost does not disclose the use of zinc and hydrochloric acid in a process which uses dehydration and hydrogenation, contrary to the Examiner's assertion.

Indeed, Bost specifically discloses the word "or" at column 2, line 62, after reaction 4 (which is the reaction that uses zinc and hydrochloric acid) and before reaction 5 (the dehydration reaction) and reaction 6 (the hydrogenation reaction).

Further, the example disclosure at column 4, line 50 to column 5, line 3 cited by the Examiner only involves the direct reduction method using zinc and hydrochloric acid; the presence of hydrogen itself is not disclosed.

Accordingly, it is submitted that the Examiner's reliance on the disclosure at column 2, lines 45-68, and at column 4, line 50 to column 5, line 3, for a single reaction scheme in which zinc and hydrochloric acid are used together with dehydration and hydrogenation is improper, and that Bost neither teaches nor suggests the present invention, such that the present invention is not anticipated by (or obvious over) Bost.

As discussed above, the reaction of the present invention is completely different from the one set forth in Bost, and is not obvious over the description of Bost. Accordingly, Applicants submit that the present invention is patentable over Bost, and withdrawal of this rejection is respectfully requested.

Obviousness Rejections of Claims 2 and 4

On page 3 of the Office Action, claim 2 is rejected under 35 U.S.C. 103(a) as being unpatentable over Bost (US 3,963,571) and Nakajima et al (US 5,300,654) in combination. Further, on page 4 of the Office Action, claim 4 is rejected under 35 U.S.C. 103(a) as being unpatentable over Bost and Nakajima et al as applied to claim 2 above, and further in view of Makita (JP 202220361).

Applicants respectfully submit that claims 2 and 4 are not obvious over the cited art combinations, and request that the Examiner reconsider and withdraw these rejections in view of the following remarks.

1) What is described in Nakajima is a dehydration reaction, and, as the Examiner admits, is different from the direct reductive reaction disclosed by Bost.

In addition, as stated previously, hydrochloric acid cannot be regarded as a reaction catalyst in the direct reductive reaction using zinc and hydrochloric acid.

Accordingly, it is evident that the hydrochloric acid used for the direct reductive reaction set forth in Bost is not equivalent to the dehydration catalyst disclosed by Nakajima.

2) On the other hand, as stated above, not only has no catalytic hydrogenation reaction with use of zinc and/or hydrochloric acid been known, but also zinc and/or hydrochloric acid in the reaction set forth in Bost cannot be regarded as catalysts.

Accordingly, it is evident that the zinc used for the direct reductive reaction set forth in Bost is not equivalent to the catalyst such as palladium, etc. set forth in Makita.

3) As has been discussed hereinabove, it is evident that those skilled in the art have no motivation for combining the catalyst of Nakajima or Makita with the reaction set forth in Bost.

Thus, Applicants submit that the method of the present invention is a new and unobvious one in which a dehydration reaction and a hydrogenation reaction are catalytically conducted in the coexistence of an acid catalyst and a hydrogenation catalyst and in the presence of hydrogen, i.e., in which the two reactions are conducted simultaneously in a single pot, thereby achieving the advantageous effect of efficient production of the ketone in concern with a high yield.

Since Nakajima and Makita do not make up for the deficiencies of Bost, it is submitted that claims 2 and 4, which depend on claim 1, are not obvious for at least the reasons given above with respect to claim 1.

As discussed above, the reaction in the present invention is completely different from that of Bost, and the method of the present invention is not described in Bost, Nakajima and Makita, so Applicants submit that the present invention would not have been reached even if Nakajima and Makita were combined with Bost. Accordingly, withdrawal of these rejections is respectfully requested.

Obviousness Rejection of Claims 5 and 6

On page 4 of the Office Action, claims 5 and 6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Bost et al and Nakajima et al and further in view of Makita.

In response, Applicants submit that for the same reasons as those set forth above, the present invention would not have been attained even if Bost, Nakajima and Makita were

combined together. In this regard, it is submitted that when the teachings of the cited art are

fairly considered, Nakajima and Makita do not make up for the deficiencies of Bost as discussed

above. Accordingly, withdrawal of this rejection is respectfully requested.

Conclusion

In view of the above, reconsideration and allowance of this application are now believed

to be in order, and such actions are hereby solicited. If any points remain in issue which the

Examiner feels may be best resolved through a personal or telephone interview, the Examiner is

kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue

Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any

overpayments to said Deposit Account.

Respectfully submitted,
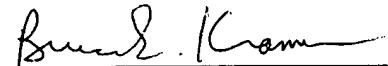
SUGHRUE MION, PLLC   Bruce E. Kramer
Telephone: (202) 293-7060   Registration No. 33,725
Facsimile: (202) 293-7860

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Date: October 28, 2005

3. Methods of Preparation

1,2-Cyclodecanediol has been prepared by the hydrogenation of sebacoin in the presence of Raney nickel[3] or platinum,[4] by the reduction of sebacoin with aluminum isopropoxide[4] or lithium aluminum hydride,[4] and by the oxidation of cyclodecene with osmium tetroxide and pyridine.[5]

[1] Cornell University, Ithaca, New York.

[2] Org. Syntheses Coll. Vol. 2, 162 (1943), Note 1f.

[3] Prelog, Schenker, and Günthard, Helv. Chim. Acta, 35, 1598 (1952); Prelog, Urech, Bothner-By, and Würsch, Helv. Chim. Acta, 38, 1095 (1955).

[4] Blomquist, Burge, and Sucsy, J. Am. Chem. Soc., 74, 3636 (1952).

CYCLODECANONE *

Submitted by Arthur C. Cope, John W. Barrett, and Ronald Dean Smith.[1]

Checked by N. J. Leonard and J. C. Little.

1. Procedure

A 1-l. round-bottomed three-necked flask is fitted with a sealed stirrer (Note 1), a dropping funnel, and a reflux condenser, through which a thermometer extends nearly to the bottom of the flask. In the flask are thoroughly mixed 40.5 g. (0.62 g. atom) of zinc dust (Note 2) and 100 ml. of glacial acetic acid, and to this mixture is added 42.5 g. (0.25 mole) of sebacoin (p.840) (Note 3). The mixture is stirred rapidly, and 90 ml. of concentrated c.p. hydrochloric acid is added dropwise during a period of 5 to 10 minutes, or as fast as control of foaming and temperature permits. The temperature must be kept between 75 and 80° (Note 4), and cooling by a water bath may be necessary during the addition of the hydrochloric acid. Stirring is continued for 1.5 hours at 75–80°. Thirty minutes after the initial addition of hydrochloric acid, and again 30 minutes later, 90-ml. portions of concentrated hydrochloric acid are added to

the mixture while the temperature is maintained at 75–80°. After the reaction is complete, the remaining zinc is separated from the cooled mixture by decantation (Note 5). The liquid phase is diluted with 700 ml. of saturated aqueous sodium chloride solution and extracted with four 250-ml. portions of ether, each of which is first used to wash the residual zinc (Note 6). The ether extracts are combined and washed with 250 ml. of saturated sodium chloride solution, three 250-ml. portions of 10% sodium carbonate solution (foaming!), and finally 250 ml. of saturated sodium chloride solution. The ethereal solution is dried over anhydrous magnesium sulfate (about 25 g. is needed). After the drying agent has been removed by filtration and the solvent by distillation, the residue is distilled at reduced pressure through an efficient column (Note 7). After a small fore-run consisting mostly of cyclodecane, cyclodecanone is collected at 99–101°/8 mm. The yield is 29–30 g. (75–78%), n_D^{25} 1.4808–1.4810 (Note 8).

2. Notes

1. A metal stirrer must not be used. A simple glass stirrer with a ball-joint seal is satisfactory.

2. Mallinckrodt technical grade may be used.[2] If Mallinckrodt analytical reagent zinc dust is used, the reaction temperature must be maintained at 50–55° instead of 75–80°.

3. Pure sebacoin gives a colorless product. A sebacoin-sebacil mixture must first be purified by recrystallization from pentane as described (p.841). The sebacil apparently is not reduced completely according to the accompanying directions and thus may contaminate the product (see Note 7).

4. The reaction temperature is important. At temperatures below 75° some sebacoin remains unreduced, while at temperatures above 80° considerable cyclodecane is formed. The submitters report that the reaction run at the reflux temperature gives cyclodecanone in 27% yield and cyclodecane in 32% yield.

5. The product should be isolated and distilled as quickly as possible inasmuch as the unreacted sebacoin is readily oxidized to sebacil, which cannot be separated from the cyclodecanone by simple distillation.

6. The residual zinc may be pyrophoric.

7. For efficient separation of cyclodecanone from cyclodecane, a 60-cm. column of the simple Podbielniak type[3] may be used. Removal of sebacil cannot be accomplished readily by fractional distillation, since cyclodecanone and sebacil have virtually identical boiling points.

8. Cyclodecanone regenerated from its semicarbazone, m.p. 203.5–205.5°, has n^{25}_D 1.4806.

3. Methods of Preparation

The procedure described is a modification of the directions of Prelog, Frenkiel, Kobelt, and Barman.[4] Cyclodecanone has been prepared by the dehydration of sebacoin followed by catalytic hydrogenation,[5] by the pyrolysis of the thorium or yttrium salt of nonane-1,9-dicarboxylic acid,[6] and by the ring enlargement of cyclononanone,[7] as well as by the reduction of sebacoin.[8]

[1] Massachusetts Institute of Technology, Cambridge 39, Massachusetts.
[2] Brown and Borkowski, J. Am. Chem. Soc., 74, 1901 (1952).
[3] Cason and Rapoport, Laboratory Text in Organic Chemistry, 2nd. ed., p. 294, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.
[4] Prelog, Frenkiel, Kobelt, and Barman, Helv. Chim. Acta, 30, 1741 (1947).
[5] Stoll, Helv. Chim. Acta, 30, 1837 (1947).
[6] Ruzicka, Stoll, and Schinz, Helv. Chim. Acta, 9, 249 (1926); 11, 670 (1928).
[7] Kohler, Tishler, Potter, and Thompson, J. Am. Chem. Soc., 61, 1057 (1939).
[8] Blomquist, Burge, and Sucsy, J. Am. Chem. Soc., 74, 3636 (1952).

CYCLOHEPTANONE *

1. NITROUS ACID METHOD
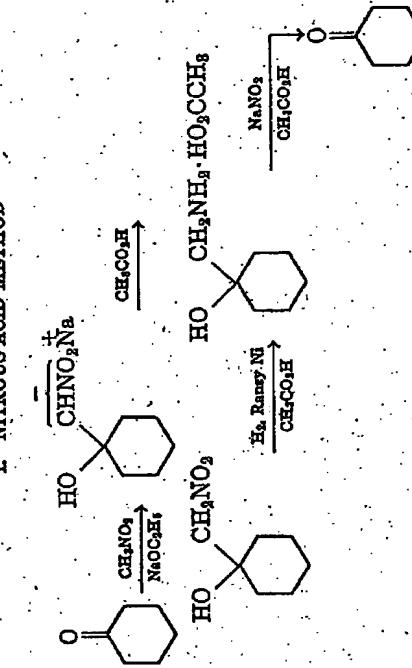
Submitted by Hugh J. Dauben, Jr., Howard J. Ringold, Robert H. Wade, David L. Pearson, and Arthur G. Anderson, Jr.[1]
Checked by Arthur C. Cope, Warren N. Baxter, and Robert J. Cotter.

1. Procedure

Caution! The sodium salt of 1-(nitromethyl)cyclohexanol may be an explosive (Note 1).

A solution of sodium ethoxide is prepared by adding 57.5 g. (2.5 g. atoms) of clean sodium to 1.2 l. of absolute ethanol (Note 2) in a 3-l. three-necked flask equipped with an Allihn reflux condenser fitted with a drying tube, a large sturdy sealed Hershberg stirrer, and a dropping funnel. After the sodium has dissolved, the solution is cooled to 40° and the condenser is replaced by a thermometer extending into the liquid. A mixture of 245.5 g. (258.5 ml., 2.5 moles) of redistilled cyclohexanone and 198 g. (175 ml., 3.25 moles) of redistilled nitromethane (Note 3) is added dropwise with vigorous stirring over the course of about 3 hours at a rate that maintains an internal temperature of 45 ± 3° (Note 4). After addition is complete, the white, pasty mass is stirred for an additional 3 hours without cooling or heating and

COMPREHENSIVE
ORGANIC
TRANSFORMATIONS

A Guide to
Functional Group Preparations

Second Edition

By
Richard C. Larock

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$$X \xrightarrow{\text{HCO}_2\text{H}}{\text{cat Pd-C}} \text{NH}_2$$
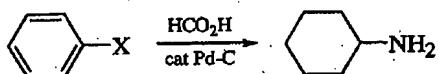
X = NO, N$_3$, NO$_2$, NH$_2$, NR$_2$

TL *33* 7477 (1992)

$$\xrightarrow[\text{cat Nb(OC}_6\text{H}_3\text{Ph}_2\text{-2,6)}_2\text{(CH}_2\text{C}_6\text{H}_4\text{Me-4)}_3]{\text{H}_2}$$
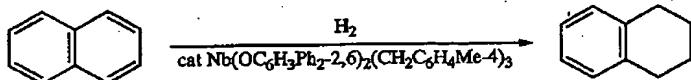
JACS *114* 1927 (1992)

3. Alkenes

$$\text{C}=\text{C} \longrightarrow \overset{\overset{\text{H}}{|}}{\underset{|}{\text{C}}} \overset{\overset{\text{H}}{|}}{\underset{|}{\text{C}}}$$
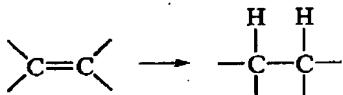
3.1. Catalytic Hydrogenation

Reviews:

R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York (1965)

P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York (1967)

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley-Interscience, New York (1971), Chpt 9

B. R. James, "Homogeneous Hydrogenation," J. Wiley, New York (1973)

F. J. McQuillin, "Homogeneous Hydrogenation in Organic Chemistry," D. Reidel, Boston (1976)

A. P. G. Kieboom and F. van Rantwijk, "Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry," Delft University Press, Delft (1977)

M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley & Sons, New York (1978), Chpt 4

Syn 85 (1981) (homogeneous asymmetric hydrogenation)

Chem Rev *85* 129 (1985) (heterogeneous catalytic transfer hydrogenation)

"Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1985), Vol 5, Chpts 2, 3, 10

P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 2

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Parts 3.1 and 3.2, pp 417–470

3.1.1. Selective hydrogenation catalysts

5% Ru on Norit	JOC *24* 708 (1959)
RuCl$_2$(PPh$_3$)$_3$	CL 1083 (1977) (polyenes to monoenes)
NaBH$_4$, CoCl$_2$ (mono > di > tri > tetrasubstituted)	JOC *44* 1014 (1979) JACS *108* 67 (1986)
Rh-C	TL *32* 2735 (1991) (fluoroalkenes); *36* 7949 (1995) (enamide)
Rh-Al$_2$O$_3$	Org Syn Coll Vol *6* 371 (1988) TL *29* 3171 (1988)

ClRh(PPh₃)₃ (Wilkinson's catalyst)

Discuss Faraday Soc 46 60 (1968)
Chem Rev 21 73 (1973)
Syn 329 (1978)
Prog Inorg Chem 28 63 (1981)

ClRh[P(p-Tol)₃]₃ (regioselective)

TL 33 5547 (1992)

[Rh(NBD)(dppb)]BF₄

CC 348 (1982) (syn to allylic, homoallylic OH)
JACS 106 3866 (1984) (syn to OH); 107 4339 (1985)
(syn to OH); 108 2476 (1986); 112 5290 (1990)
(homoallylic OH)
TL 25 4637 (1984) (allylic OH); 26 6005 (1985)
(homoallylic OH); 28 3659 (1987)

[Rh(COD)(dppb)]BF₄

JACS 115 7152 (1993)
TL 34 4939 (1993)

[Rh(NBD)(dppb)]OTf

Org Syn Coll Vol 8 420 (1993)

[Ir(COD)(dppb)]BF₄

TL 25 4637 (1984) (allylic OH)

[Ir(COD)(py)(PCy₃)]PF₆

TL 22 303 (1981) (α face of steroids); 25 4637
(1984) (allylic, homoallylic OH); 26 6005 (1985)
(homoallylic OH)
JACS 105 1072 (1983) (syn to OH); 106 3866
(1984) (syn to OH); 109 6493 (1987) (syn to
CONR₂); 113 4926, 4931 (1991) (syn to
CONR₂)
Organomet 2 681 (1983) (syn to OH)
JOC 50 5905 (1985) (syn to CO₂R, CONR₂); 51
2655 (1986) (syn to OH, CO₂R, C=O, OMe); 60
5102 (1995) (syn to OH)

Nickel boride (P-2)

JOC 38 2226 (1973); 46 1263 (1981)

LaNi₅H₆

JOC 52 5695 (1987) (least substituted double
bond)

NaH, NaO-t-Am, Ni(OAc)₂

JOC 45 1937, 1946 (1980)

Pd-C

TL 32 2735 (1991) (fluoroalkenes)

Pd-BaSO₄

TL 32 2735 (1991) (fluoroalkenes)

Montmorillonite-PPh₂·PdCl₂

TL 33 121 (1992)

Pd(hfacac)₂, Me₃Si(OSiHMe)ₙOSiMe₃

TL 34 3075 (1993)

PtCl₂, (Et₄N)SnCl₃ or (Ph₃PMe)SnBr₃

JACS 94 8716 (1972) (polyene to monoene)

PtO₂

Adv Catalysis 9 727 (1957)

## 3.1.2. Enantioselective hydrogenation catalysts

Reviews:

H. B. Kagan, "Comprehensive Organometallic Chemistry," Eds. G. Wilkinson and F. G. A. Stone,
Pergamon, Oxford (1982), Vol 8, p 463
Pure Appl Chem 56 99 (1984)
"Asymmetric Catalysis," Ed. B. Bosnich, NATO ASI Ser. E, No. 103, Martinus Nijhoff, Dordrecht
(1986), Chpt 2
Chem Rev 92 1051 (1992) (asymmetric)

SL 169 (1992) (Rh bis-phosphines)

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 1

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21d, G. Thieme, Stuttgart–New York
   (1995), p 4239

Catalyst	Substrate	
Ti(BINOL), n-BuLi, PhSiH$_3$	trisubstituted aryl alkenes	JACS *115* 12569 (1993)
Ru(DIPAMP)(2-Me-allyl)$_2$ or Ru$_2$X$_2$(DIPAMP)	α,β-unsaturated carboxylic acids, α-amido acrylic acid	TL *33* 5343 (1992)
Ru(2-Me-allyl)(diphosphine)	α,β-unsaturated carboxylic acid	Tetr Asym *2* 43 (1991)
Ru$_2$Cl$_4$(BINAP)	α-amido-α,β-unsaturated lactam	TL *35* 3239 (1994)
	enones	JOC *60* 357 (1995)
Ru$_2$Cl$_4$(BINAP)$_2$(NEt$_3$)	α-amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL *28* 1905 (1987); *35* 835 (1994)
	α,β-unsaturated lactone and anhydride	TL *33* 635 (1992)
	α-alkylidene lactams	TL *36* 7379 (1995)
	2-fluoro-2-alkenoic acids	TL *33* 7877 (1992)
	enones	JOC *60* 357 (1995)
	vinylic ester	JOC *60* 357 (1995)
	vinylic ether	JOC *60* 357 (1995)
[(arene)RuX(BINAP)]X	allylic alcohol, α,β-unsaturated carboxylic acid	CC 1208 (1989) JOC *59* 3064 (1994)
	α,β-unsaturated lactone, enone	TL *33* 635 (1992) JOC *60* 357 (1995)
Ru(BINAP)(Ph)Cl	enamide	JOC *60* 4324 (1995)
RuHCl(BINAP)$_2$	α-amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL *28* 1905 (1987)
Ru(OAc)$_2$(BINAP)	enamides	JACS *108* 7117 (1986) JOC *59* 297 (1994)
	allylic alcohols	JACS *109* 1596 (1987) JOC *53* 708 (1988) TL *34* 7359 (1993)
	homoallylic alcohols	JACS *109* 1596 (1987)
	enone	TL *33* 635 (1992) JOC *60* 357 (1995)
	α-amido acrylate esters	JOC *59* 3676 (1994)
	vinylic ether	JOC *60* 357 (1995)
	vinylic ester	JOC *60* 357 (1995)
	α,β-unsaturated carboxylic acid	JOC *52* 3174 (1987) TL *31* 7189 (1990) SL 501 (1994)

Catalyst	Substrate	
Ru(OAc)$_2$(BINAP) *(continued)*	β,γ-unsaturated carboxylic acids	JOC *52* 3174 (1987) TL *31* 7189 (1990)
Ru(OAc)$_2$(tolbinap)	allylic alcohols	TL *31* 549 (1990)
Ru(OAc)$_2$(H$_8$-BINAP)	α,β-unsaturated carboxylic acid	SL 501 (1994)
Ru(O$_2$CCF$_3$)$_2$(BINAP)	allylic alcohols	TL *29* 5343 (1988)
[Rh(NBD)Cl]$_2$, Ph$_2$PCH$_2$CH(CH$_3$)PPh$_2$	α-amidoacrylic acids and esters	JOC *56* 1783 (1991)
[Rh(NBD)$_2$]ClO$_4$, Ph$_2$PCH$_2$CH(CH$_3$)PPh$_2$	α-amidoacrylic acids and esters	JACS *110* 5491 (1978)
[Rh(COD)Cl]$_2$, norphos	α-amidoacrylic acid	Angew Int *18* 620 (1979)
[Rh(NBD)Cl]$_2$, norphos	α-amidoacrylic acid and ester	JOC *56* 1783 (1991)
[Rh(NBD)Cl]$_2$, *S,S*-chiraphos	α-amidoacrylic acid	JOC *56* 1783 (1991)
[Rh(NBD)(*S,S*-chiraphos)]ClO$_4$	α-amidoacrylic acids and esters	JACS *99* 6262 (1977); *115* 4040 (1993) JOC *52* 5143 (1987)
[Rh(NBD)(BINAP)]ClO$_4$	α-amidoacrylic acids α-amidoacrylic acids and esters	JACS *102* 7932 (1980) Tetr *40* 1245 (1984)
[Rh(NBD)(BINAP)]BF$_4$	α,β-unsaturated ester	JACS *108* 2476 (1986)
(binaphthyl-P(Cy$_2$)$_2$)Rh(NBD)X (X = Cl, ClO$_4$)	α-amidoacrylate ester, itaconic acid and ester	TL *32* 4745 (1991)
[Rh(NBD)(Josiphos)]BF$_4$	α,β-unsaturated ester, α-amidoacrylate ester	JACS *116* 4062 (1994)
[Rh(NBD)(diPAMP)]BF$_4$	α-amidoacrylamide	TL *35* 5785 (1994)
[Rh(NBD)(Ph-CAPP)]BF$_4$	α-amidoacrylamide	TL *35* 5785 (1994)
[Rh(COD)(o-(PC$_6$H$_4$P) phospholane, R = Me, Et, Pr, *i*-Pr)]OTf	α-amidoacrylate esters, enol acetates	JACS *113* 8518 (1991); *115* 10125 (1993); *116* 10847 (1994); *117* 9375 (1995)
[Rh(COD)(o-(PC$_6$H$_4$P) Me$_2$/Me$_2$ phospholane)]OTf	α-amidoacrylate ester	JACS *117* 9375 (1995)
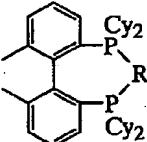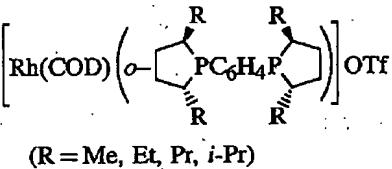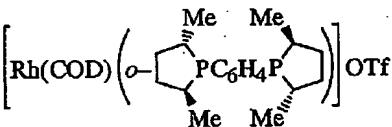
Catalyst	Substrate	Reference
$[Rh(COD)(PC_5H_4FeC_5H_4P)]OTf$ structure $(R = Me, Et)$	α-amidoacrylate ester, α,β-unsaturated ester	TL *35* 9363 (1994)
[Rh(COD)(anthraphos)]BF$_4$	α-amidoacrylic acid	TL *35* 7593 (1994)
[Rh(COD)(o-EtC$_6$H$_4$PPhCH$_2$CH$_2$PPh-C$_6$H$_4$Et-o)]BF$_4$	α-amidoacrylic acids and esters	TL *36* 8271 (1995)
[Rh(COD)$_2$]BF$_4$, R$_2$PCHMeFer-FerCH-MePR$_2$	α-amidoacrylate esters	JACS *117* 9602 (1995)
[Rh(COD)$_2$]ClO$_4$, (PPh$_2$ / PPh$_2$ structure)	α-amidoacrylic acid	SL 49 (1991)
[Rh(COD)Cl]$_2$, (Ph$_2$P / PPh$_2$ N-Boc structure)	acrylic acid	SL 155 (1993)
[(COD)Rh(Ph$_2$P... P Ph$_2$ NCONHPh)]BF$_4$	acrylic acid	SL 155 (1993)
[RhL(COD)]SbF$_6$ (L = glucose 3,4-diphosphinites)	α-amidoacrylic acids and esters	JACS *116* 4101 (1994)
Rh(O$_2$CCF$_3$)$_2$(tolbinap)	enamides	TL *28* 4829 (1987)
chiral (aminoalkyl)ferrocenylphosphine-Rh	trisubstituted acrylic acids	JACS *109* 7876 (1987) TL *29* 5969 (1988)
chiral pyrrolidinodiphosphines-Rh	itaconic acid; α,β-unsaturated acids, esters, and ketones; α-amidoacrylic acids	CL 567 (1978) Ber *119* 3326 (1986) Angew Int *27* 1180 (1988) Syn 743 (1989) JOMC *387* 209 (1990) TL *32* 3671 (1991) JACS *115* 152 (1993)
diop-Rh	α,β-unsaturated carboxylic acids, α-amidoacrylic acids and esters	CC 481 (1971) JACS *94* 6429 (1972) JOC *56* 1783 (1991)
Ar$_2$PCH$_2$CH-CHCH$_2$PAr$_2$-Rh (dioxolane structure)	α,β-unsaturated ester	TL *29* 4755 (1988); *30* 735 (1989); *31* 261 (1990) JOC *60* 4339 (1995)
Ph, HO, O, PPh$_2$ / PPh$_2$-Rh (structure)	α-amidoacrylic acid and ester	TL *35* 6071 (1994)
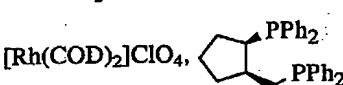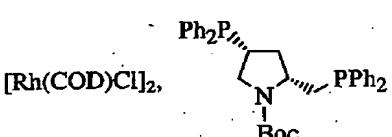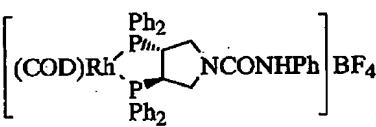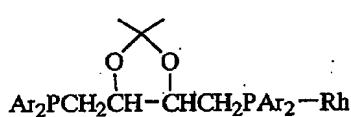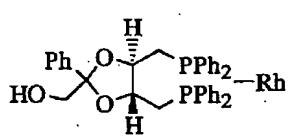
Catalyst	Substrate	
$Ph_2PCH(CH_2OR)CH_2PPh_2$-Rh	α-amidoacrylic acids and esters	J Chem Res (S) 117 (1982)
o-Ph(Me)PC$_6$H$_4$P(Me)Ph-Rh(I)	α-amidoacrylate ester	JACS *115* 4040 (1993)
{R,R-1,2-bis((phenyl-o-anisoyl)-phosphino)-ethane}-Rh(I)	various α-amidoacrylate derivatives	JACS *99* 5946 (1977); *109* 1746 (1987); *115* 4040 (1993)
organosamarium compound	alkenes	JACS *114* 2761 (1992)

3.2. Diimide Reduction (HN=NH)

J Chem Ed *42* 254 (1965) (review)

Angew Int *4* 271 (1965) (review)

Syn Commun *12* 287 (1982) (HONH$_2$, EtOAc)

JOC *52* 4665 (1987); *57* 6092 (1992) (both TsNHNH$_2$, NaOAc); *59* 4346 (1994) (N$_2$H$_4$, NaIO$_4$)

JACS *110* 1529 (1988) (N$_2$H$_4$, air, CuSO$_4$)

Org Rxs *40* 91 (1991) (review)

TL *34* 4137 (1993)
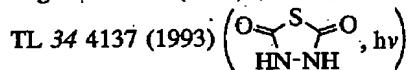
3.3. Hydroboration–Protonolysis

$$RCH{=}CH_2 \begin{array}{c} \xrightarrow[\text{2. HO}_2CC_2H_5]{\text{1. BD}_3} RCHDCH_3 \\ \xrightarrow[\text{2. DO}_2CC_2H_5]{\text{1. BH}_3} RCH_2CH_2D \end{array}$$
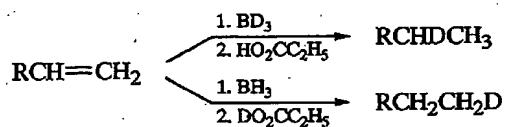
JACS *81* 4108 (1959)

JOMC *255* 135 (1983)

3.4. Metal Hydrides

LiH, VCl$_3$ (RCH=CH$_2$ only)	JOC *45* 1041 (1980)
NaH, NaO-t-Bu, FeCl$_3$	TL 3947 (1977)
NaH, NaO-t-Am, Ni(OAc)$_2$	TL 1069 (1977)
NaBH$_4$, CoCl$_2$	JACS *108* 67 (1986)
NaBH$_4$, cat NiCl$_2$·6H$_2$O	JACS *104* 5781 (1982) JOC *56* 1192 (1991)
NaBH$_3$CN, HCl	JACS *113* 5775 (1991)
LiAlH$_4$	TL *31* 553 (1990)
LiAlH$_4$, TiCl$_4$ or ZrCl$_4$	TL 15 (1976) JOMC *142* 71 (1977)